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(19) (CA) **CANADIAN PATENT** (12)

(54) Dispersion Based on Self-Hardening Mixtures, Process
for Preparing It and the Use Thereof

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Dispersion based on self-hardening mixtures, process for
preparing it and the use thereof

5 It is known to produce dispersions which can be used
as lacquers or paints. The epoxy groups of a mixture of
epoxy resin based on diphenylolpropane and epichlorohydrin
and polyadducts of castor oil and epoxy resins based on
the products mentioned above are reacted with secondary
amines, mixed with resols which contain dimethylene ether
bridges or those obtained from diphenylolpropane and
formaldehyde, after etherification of the methylol groups
with alcohols, the bases are neutralised, the mixtures in
10 organic solvents are mixed with water and the organic
solvent is eliminated, possibly after the addition of
dispersants or agents for improving surface properties.
This process has proved satisfactory, but there was a
desire to improve the dispersions and the preparation
15 thereof so as to improve the coatings obtained from them
and for reasons of reliability. The aim of the present
invention is therefore to make the castor oil component
superfluous in dispersions obtained from mixtures of epoxy
resins and phenolic resins.

20 It is also known to prepare non-ionic phenolic resin
dispersions which may contain plasticising substances, including
epoxy resins. These dispersions consist of polyphenols
based on phenol or substituted phenols and formaldehyde,
which are substituted with methylol groups. These
25 dispersions, which can harden without giving rise to the formation of
harmful substances, may also be plasticised by the addition of epoxy resins.
However, in this dispersing process, it is not possible to
use long-chained epoxy resins. Instead, epoxy resins which
are liquid at ambient temperature, owing to their low
30 molecular weight, or which have a very low melting point
and therefore give only a reduced plasticising effect,



must be used. The use of higher molecular epoxy resins is ruled out, owing to their excessively high melting viscosity. Therefore, these resins are not dispersible. Moreover, non-ionic dispersions cannot be deposited either by the addition of basic substances or by the application of electric current. Thus, they are unsuitable for modern methods of application, for example paint application by electrodeposition.

Another publication describes the preparation of water-soluble phenolic resins which harden without giving rise to the formation of harmful substances, based on methylol compounds of polyphenols, namely ortho- structured novolaks. However, these resins cannot be plasticised. In order to convert them into aqueous solutions they have to be used as alkali phenolates. Alkaline aqueous phenolic resin solutions of this kind are not suitable for use in paints or lacquers since they do not yield a cohesive film and the coatings are water-soluble and brittle.

An aqueous mixture is also known (German OLS 2 415 100), consisting of a) a reaction product of a special formula of a polyepoxide with a mono- or dialkanolamine, b) a thermosetting phenolic or amine resin and c) water or a water-dilutable liquid. As the formula and examples show, in the reaction product a) the amine group is converted into a salt by means of an inorganic or carboxylic acid. This publication gives no details of the chemical structure of the phenolic resin component b). However, if conventional phenolic resins are used, there is the disadvantage that the hardening is not rapid enough and, during hardening, phenol and formaldehyde may be split off, leading to pollution of the environment.

The present invention aims to overcome these difficulties.

It has now been found that the above-mentioned disadvantages are avoided with a dispersion based on self-hardening mixtures of A) epoxy resins formed from diphenylol alkane and epihalohydrin and B) phenolic resins in the

form of methylol compounds of substituted polyphenol compounds based on a mixture of substituted and unsubstituted phenols on the one hand and formaldehyde on the other hand in a weight ratio of A) : B) of from 10:90 to 90:10, preferably 20:80 to 80:20, which is characterised in that the dispersion capable of being deposited with bases or electric current contains a reaction product which has been prepared from an epoxy resin A) with an average molecular weight of from 300 to 30,000, preferably 500 to 20,000, with C) a secondary amine which is thus present as a tertiary amine in the reaction product and is converted into a salt therein with an inorganic acid or monocarboxylic acid D), the amine C) being reacted in an amount of from 10 to 100, preferably from 35 to 100 equivalent-percent per epoxy group, whilst the equivalent ratio between the tertiary amine group and the acid is (25 to 200) : 100, preferably (50 to 175) : 100.

The term "dispersion" refers to dispersed systems, including both dispersions in the stricter sense and also colloid systems. Usually, the colloids in the colloid systems, i.e. colloid solutions, have an average particle size of about 10^{-4} to 10^{-6} mm. Dispersed systems having a particle size above this range are dispersions in the stricter sense of the word.

If the dispersion according to the invention is present in the form of a dispersion in the stricter sense, it preferably contains a reaction product of the epoxy resin A) with an average molecular weight of from 1000 to 30,000, preferably from 2000 to 20,000. If it is present in the form of a colloid solution, it preferably contains a reaction product of the resin A) with an average molecular weight of from 300 to 30,000, preferably from 500 to 20,000.

Surprisingly, no toxic harmful substances are split off in the hardening of the dispersion according to the invention. Moreover, the hardened products obtained from the dispersions according to the invention do not have any

substances which affect smell or taste. Therefore, the dispersions according to the invention are also suitable, for example, for the internal coating of food packages.

5 The invention also provides a process for preparing the above-mentioned dispersion, which is characterised in that the epoxy resin A) is reacted with the secondary amine C) to form a tertiary amine, whereupon the tertiary amine is dissolved in at least one organic solvent, which is preferably polar and partially water-miscible, and is
10 converted with the acid D) into a salt, and in that before, during or after the salt formation with the acid at least one phenolic resin B) is added, the resulting solution is mixed with water to form a dispersion and, in the case of the preparation of a dispersion in the stricter
15 sense, the organic solvent is then eliminated, and in that the amine is used in an amount of 10 to 100, preferably 35 to 100 equivalent-% per epoxy group, and the equivalent ratio between the tertiary amine group and the acid is (25 to 200) : 100, preferably (50 to 175) : 100.

20 Examples of epoxy resins A) are the standard commercial epoxy resins, particularly those based on diphenylol alkanes such as diphenylolmethane (bisphenol F) and preferably diphenylolpropane (bisphenol A) on the one hand and epihalohydrin and/or methyl epihalohydrin, such as
25 epibromohydrin, preferably epichlorohydrin, which can be prepared by the one-stage or two-stage process described in the literature (see for example "Epoxydverbindungen und Epoxydharze", Paquin, 1958, page 322 ff.); e.g. those with a Durrans softening point (SP) of at least 70°C and an
30 epoxy equivalent weight (EE) of at least 180, more particularly for colloid systems, and at least 490 for dispersions in the stricter sense; for example, products with a SP of 93 to 104°C and EE 875 to 1000 and SP 118°C and EE 1865 may be used.

35 Examples of phenolic resins B) are methylol compounds, particularly those polyphenol compounds which, in the case of the dispersion in the stricter sense, contain alkyl,

alkenyl, aryl and/or aralkyl groups as substituents and, in the case of the colloid solution, contain hydrophilic groups such as hydroxyalkyl groups, e.g. mono- or polyhydroxyalkyl groups as substituents, the proportion thereof being 5 to 100, preferably 10 to 90 equivalent-%, more particularly 10 to 80 equivalent-% in colloid systems and 20 to 90 equivalent-% in non-colloid systems, based on the phenolic OH groups. Substitution may be effected both at the nucleus and also at the phenolic OH groups or at both.

The phenolic resins B may appropriately be prepared in several stages, the first stage being condensation to form a substituted polyphenol linked with methylene bridges, namely a novolak. The degree of condensation of this novolak is generally in the low to middle range, whilst the molar ratio between the sum of the total phenols and formaldehyde in the starting substances is 1 : (0.1 to 0.7), preferably 1 : (0.2 to 0.65). It is possible to prepare the novolak initially from phenol and formaldehyde, then distil off the unreacted phenol and then carry out substitution, preferably alkoxylation or alkylation. This method is particularly recommended if the substituting reagent, e.g. alkylating reagent, can be substituted particularly easily at the nucleus, as is the case, for example, with vinyl aromatic compounds or terpenes. Catalysts which may be used for the novolak formation are protonic acids such as sulphuric, phosphoric or hydrochloric acid, or Lewis acids such as boron fluoride or metal phenols such as aluminum phenolate.

In the subsequent substitution of the phenolic resin, the following substituents may be incorporated in order to prepare dispersions in the stricter sense: straight-chained or branched alkyl groups with 1 to 18, preferably 4 to 12 carbon atoms, such as n-butyl, tertiary or secondary butyl, the various octyl, nonyl and dodecyl groups; cycloaliphatic compounds such as cyclohexyl; alkenyl groups such as allyl, isopentenyl, isobutenyl, C₁₄-alkenyl groups as found in cashew nut oil; terpene groups; aryl groups

such as phenyl; aralkyl groups derived from styrene, α -methylstyrene and vinyl toluene. The substitution at the phenolic OH group may be effected in conventional manner by etherification of the phenolic OH groups, e.g.
5 by Williamson synthesis.

On the other hand, substituted novolaks may also be prepared by co-condensation of the substituted phenol with non-substituted phenol and formaldehyde.

Examples of substituted phenols are: alkylphenols, particularly p-alkylphenols, such as p-propyl- and iso-propylphenol, p-tert-butylphenol, p-octyl- and iso-octylphenol, p-nonyl- and iso-nonylphenol, p-dodecylphenol, p-phenylphenol or p-cyclohexylphenol, and also phenols substituted with vinyl aromatic compounds, particularly
10 styrene.
15

In order to prepare colloid solutions, the hydrophilic substitution of the polyphenol may be effected by reacting the phenolic OH groups with monoepoxides such as ethylene oxide, propylene oxide, styrene oxide, etc., glycidol,
20 phenylglycidolethers, etc. However, it may also be carried out using halohydrins such as ethylene chlorohydrin, propylene chlorohydrins, dichloropropanol and monochloro-propyleneglycol. Finally, the nuclear substitution with
25 oxo compounds, particularly formaldehyde, leading to alkylol groups should also be regarded as hydrophilic substitution.

Instead of the substituted phenols mentioned above, it is also possible to use the methylol compounds, particularly the dimethylol compounds thereof. In calculating
30 the initial molar ratio, the reactive formaldehyde found as a methylol group must also be taken into account. After the reaction of condensation, these novolaks are also distilled carefully to remove any unreacted phenol.

The substituted novolaks obtained are subsequently
35 converted into their methylol compounds. This is done by base-catalysed reaction with formaldehyde. Suitable catalysts include, for example, alkali and alkaline earth metal compounds and

also salts such as those of the transition metals with organic acids or weak inorganic acids such as boric acid or phosphoric acid. However, it is preferable to use alkali hydroxides. The catalyst and water are added to the molten novolak, the melt is cooled to 30 to 80, preferably 40 to 70°C and the formaldehyde is added either as aqueous formaldehyde or in the form of paraformaldehyde. Before, during or after the reaction with formaldehyde, solvents which aid the process of dissolution, particularly aromatic hydrocarbons, also aromatic hydrocarbons mixed with alcohols, or alcohols themselves may be used. In the control of the reaction, any substantial etherification reaction between the methylol groups and alcohols is prevented. After all the formaldehyde has been used up, the catalyst is neutralised by the addition of an acid and the aqueous phase is removed. The salts may be filtered off after the reaction mixture has been dehydrated by distillation under reduced pressure.

Examples of amines C) include, in particular, secondary amines, such as alkyl alkanolamines and dialkanolamines, e.g. ethyl ethanolamine, ethyl isopropanolamine, diethanolamine, dipropanolamines, the lower alkyl ethers, preferably methyl and/or ethyl ethers of these amines, or other amines with a high base strength, such as dialkylamine with alkyl or alkylene groups each having up to 3 carbon atoms, e.g. dimethylamine, diethylamine, dipropylamine with decreasing activity.

The reaction between components A) and C) may generally be carried out at between ambient temperature and the boiling temperature of the solvent, preferably between 60 and 100°C; it generally lasts from 10 minutes to 2 hours.

Examples of solvents for the tertiary amine formed, for the preparation of a dispersion in the stricter sense, include, for example, the various butanols, ethyl acetate, methyl ethyl ketone, cyclohexanone, either individually or in admixture or mixtures of these solvents with a minor amount of aromatic compounds or petrol, but preferably n-

butanol. Suitable solvents in the preparation of a colloid system are solvents which are totally or partly water-miscible, e.g. glycols, glycol ethers, preferably ethylene glycol monoalkyl ethers, e.g. those with an alkyl group having from 1 to 4 carbon atoms and lower ketones.

The neutralisation of the amine adduct with acids may be carried out before, during or after the addition of the phenolic resin component. Examples of suitable acids D) for the salt formation include mineral acids such as phosphoric acid or monocarboxylic acids such as formic acid, acetic acid, sorbic acid, but preferably monocarboxylic acids containing OH groups, such as gluconic acid and/or lactic acid.

Since the phenolic resin components do not carry any alkoxymethyl groups, no alcohols can be split off during hardening.

After the addition of water and possibly dispersing agents, the solvent is distilled off as an azeotrope, preferably under reduced pressure. The water may be recycled or the quantity may be judged so that no recycling is necessary. The stability of this dispersion is surprisingly not affected, or only slightly affected, by the distillation (optionally under reduced pressure), even if temperatures of 70 to 90°C are used during the distillation, these temperatures having a favourable effect on the speed of distillation. In this way, the auxiliary solvent can be removed quantitatively.

According to one embodiment of the invention, dispersing aids, e.g. cationic or non-ionic surfactants may be added to the dispersion. Suitable dispersing agents are, for example, polyvinyl alcohol, alkoxylates of compounds containing OH groups, such as polyalcohols, phenols, esters of polyhydric alcohols or the like.

The dispersions according to the invention have the advantage that they contain only traces of unreacted starting materials. Even during thermal hardening, phenol

and formaldehyde are split off only in traces. The dispersions in the stricter sense are also free from solvents, and generally contain residual solvent only in quantities of less than 0.5 %.

5 The dispersions are elasticised epoxy resin/phenolic resin dispersions. They are cationic by nature and may therefore be precipitated by the addition of basic substances. However, they may also be deposited by electrodeposition, i.e. by cathodic precipitation, in which
10 a cohesive coating is formed at the cathode. Since they are also self-hardening, it is also possible to apply the dispersions by the roller painting method as stoving enamel or by spray coating (which may possibly be carried out by the so-called AIRLESS method) to form a coating on
15 the objects which are to be protected. The dispersions are substantially unaffected by high pressures and therefore do not present any problems caused by coagulation in the coating apparatus, as generally occurs with other dispersions, on account of their sensitivity to pressure.
20 In the thermal hardening, the stoving temperatures also depend on the nature of the anion used for neutralisation and may be between 110 and 380, preferably between 140 and 380°C, depending on the anion. The times required are between 60 minutes and a few seconds.

25 The dispersions according to the invention may be used not only for paints and coatings but also for various other purposes, e.g. as adhesion promoters for inorganic materials such as glass, asbestos and the like, as fibre sizing agents, impregnating agents, binders for abrasive
30 particles for the production of abrasives on flexible substrates or abrasive materials or the like.

 In the examples which follow T = parts by weight and % = percent by weight. Unless otherwise stated, the viscosity of the resins was determined in a 50% solution
35 in ethylene glycol monoethyl ether at 20°C. The viscosity of the dispersions was measured with the Visko- tester spindle E 30, factor 4 at 22°C.

Examples

1) Dispersion based on phenylphenol-phenol novolak and epoxy resin.

a) Preparation of the novolak

5 In a reaction vessel fitted with stirrer, thermometer, heater, cooler, distillation apparatus and apparatus for circulatory distillation under reduced pressure, 1134 T of an aqueous 37% formaldehyde solution, 600 T of xylene and 1190 T of p-phenylphenol are suspended and heated to 10 60°C. At this temperature, 420 T of 33% aqueous sodium hydroxide solution are added and reacted, with stirring, until the formaldehyde content is 0.8%. The mixture is then neutralised with 700 T of 25% sulphuric acid and 15 adjusted to pH 3.0. After settling, 1693 T of bottom liquor are separated off. The mixture is washed with water, then after separation 2632 T of phenol are added and the water formed is distilled off azeotropically under normal pressure. The temperature is increased to 220°C by removing part of the circulating xylene. 419 T of aqueous phase are 20 precipitated. Then the mixture is distilled under reduced pressure for 1 hour at 220°C and a total of 2330 T of distillate are obtained.

 In the reaction vessel there remain 2118 T of a phenyl-substituted novolak, melting point 87°C, viscosity 25 281 mPa.s/20°C (50% in ethylene glycol monoethyl ether).

b) Preparation of the methylol compound

 662 T of the novolak obtained under a) are melted; the melt is heated to 120°C. At this temperature, 240 T of 33% sodium hydroxide solution and 180 T of water are 30 added. The melt is cooled to 60°C, mixed with 227 T of aqueous 37% formaldehyde, with stirring, and then stirred at 60°C for 5 hours. After this time, no further free formaldehyde can be detected. The mixture is diluted with 520 T of isobutanol and 50 T of xylene and adjusted to pH 35 5.0 with 380 T of 25% sulphuric acid. After separation of

the bottom liquor, the mixture is washed with 500 T of water. The mixture is dehydrated by circulatory distillation at reduced pressure at a sump temperature of 50°C. 411 T of water are obtained. In the flask, 1107 T of a 66.3% resin solution are left, viscosity 4540 mPa.s/20°C.

c) Preparation of the dispersion

In a reaction vessel equipped as described above, 300 T of a standard commercial epoxy resin based on bisphenol A and epichlorohydrin with an epoxy equivalent weight of 1700 to 2000, an average molecular weight of 3400 to 4000 and a viscosity of 1750 to 2700 mPa.s/25°C (40% in ethylene glycol monobutyl ether) are melted together with 150 T of isobutanol, the melt is cooled to 80°C, mixed with 10.8 T of diethanolamine and reacted at this temperature for 1 hour. Then 302 T of the resin obtained in b), 60 T of 42% gluconic acid and 750 T of water are let in, one after the other, and the mixture is cooled to 60°C with constant stirring. Then, at reduced pressure, at a sump temperature of between 45 and 65°C, 520 T of a two-phase distillate consisting of isobutanol, xylene and water are distilled off. In the flask, a finely divided dispersion is left, solids content 57.7%, viscosity 960 mPa.s/22°C.

The dispersion is free from solvent. The isobutanol content is 0.01%. No free formaldehyde or free phenol can be detected. The dispersion can be stored at 190°C for 30 minutes and yields deformable, sterilisable coating compositions which are suitable as internal coatings for food containers.

2) Dispersion based on styrene-modified novolak and epoxy resin.

a) Preparation of the novolak

In a reaction vessel fitted with thermometer, stirrer, reflux condenser, descending cooler and vacuum device, 70 T of phenol, 0.4 T of maleic anhydride and 32.2 T of

30% aqueous formaldehyde solution are refluxed for 3 hours. Then reduced pressure is applied and the volatile constituents are distilled off up to a sump temperature of 220°C. 49.9 T of a phenol novolak with a viscosity of 290 mPa.s/20°C, 5 50% in ethylene glycol monoethyl ether, are left in the reaction vessel. The content of free phenol is 0.01%.

b) Preparation of the methylol compound

33.55 T of the novolak obtained are melted and mixed with 0.1 T of concentrated sulphuric acid. 17.22 T of 10 styrene are added to the melt, which is maintained at 80°C, the temperature is then increased to 120°C and this temperature is maintained for a further hour. Then 18.44 T of 33% sodium hydroxide solution and 14.88 T of water are added, the mixture is cooled to 60°C and mixed with 18.76 T 15 of a 37% aqueous formaldehyde solution. After 3½ hours, no further free formaldehyde can be detected. The melt is then diluted with 36.69 T of isobutanol and 4.13 T of xylene and neutralised with 16.12 T of 50% sulphuric acid. After the aqueous phase has been separated off, the mixture 20 is dehydrated as in Example 1, paragraph 2, by circulatory distillation under reduced pressure and 96 T of a 60% resin solution with a viscosity of 1150 mPa.s/20°C are obtained.

c) Preparation of the dispersion

25 In a reaction vessel equipped as described herein-before, 250 T of the epoxy resin mentioned in Example 1 are melted in the presence of 125 T of n-butanol and reacted with 10.8 T of diethanolamine as described therein. Then 410 T of the resin described in the previous paragraph and 30 58 T of 42% gluconic acid and 750 T of water are added. After stirring for half an hour, 535 T of distillate are distilled off from the resulting resin suspension, under reduced pressure, as in Example 1. The sump temperature is not more than 65°C whilst the temperature of the heating 35 agent is not more than 85°C. 1075 T of a finely divided aqueous dispersion containing a residue of 0.1% n-butanol

and 0.05% isobutanol are left in the flask. No free formaldehyde or free phenol can be detected.

20 T of a 5% aqueous polyvinyl alcohol solution are added as dispersing agent to this dispersion. This
5 polyvinyl alcohol has a degree of hydrolysis of $87.7 \pm 1\%$, an ester number of 140 ± 10 , a residual acetyl content of 10.7 ± 0.7 , an ash content of 0.5% and a viscosity of 2600 ± 150 mPa.s/20°C, measured as a 4% aqueous solution. The finished dispersion has a residue of 49% and a
10 viscosity of 390 mPa.s/22°C.

The dispersion may be used as an internal coating for food cans and may be stoved at 190°C for 30 minutes. After stoving, the coating films 4 micrometres thick obtained
15 by the centrifugal coating method are sterilisable and elastic. They do not impart any taste to the contents of the container when used as an internal coating for food containers.

3) Colloid solution based on phenol-hydroxypropyl-di-hydroxypropylphenol novolak and epoxy resin.

20 a) Preparation of the novolak

In a reaction vessel provided with thermometer, stirrer, reflux condenser, descending cooler and vacuum device, 70 T of phenol, 0.4 T of maleic anhydride and 32.2 T of 30% aqueous formaldehyde solution are refluxed
25 for 3 hours. Then reduced pressure is applied and the volatile constituents are distilled off up to a sump temperature of 220°C. 49.9 T of a phenol novolak with a viscosity of 290 mPa.s/20°C, 50% in ethylene glycol monoethyl ether, are left in the reaction vessel. The
30 content of free phenol is 0.01%.

b) Preparation of the methylol compound

1500 T of the polyphenol obtained in a) are melted and, at 110°C, 430 T of 33% sodium hydroxide and 375 T of water are added one after the other and the mixture is cooled to
35 90°C. At this temperature, 320 T of glycidol are added, this

temperature is maintained for 1 hour and then cooled to 60°C. Then 810 T of a 37% aqueous formaldehyde solution are introduced and the mixture is stirred until the formaldehyde content falls to 0. This takes about 5 hours. Then 320 T of toluene and 960 T of n-butanol are added and the mixture is adjusted to a pH of about 4.0 with 700 T of 25% sulphuric acid. After phase separation, 1478 T of bottom liquor are separated off and then washed with 600 T of a half-concentrated sodium chloride solution. A further 555 T of bottom liquor are separated off. The mixture is dehydrated under reduced pressure, whilst the solvent is recycled. About 500 T of water are separated off. After filtration 3285 T of a 67.6% resin are left, having a viscosity of 2200 mPa.s/20°C.

15 c) Preparation of the colloid solution

1100 T of the solution thus obtained are freed from solvent over a water bath at a sump temperature of 80°C, under reduced pressure, and then 150 T of ethylene glycol monoethyl ether are added.

20 2057 T of a solution obtained as follows are added to this resin solution: 1902 T of an epoxy resin based on bisphenol A and epichlorohydrin with an epoxy equivalent weight of between 900 and 1000 (commercially available product Epikote 1004 made by Shell) are dissolved in the same quantity of ethylene glycol monoethyl ether, the solution is heated to 80°C, mixed with 210 T of diethanolamine, kept at 80°C for 2 hours and then cooled. The solution obtained in a quantitative yield has a residue (1^h135°C) of 54.7% and a viscosity of 3200 mPa.s/20°C. 25 The mixture of phenolic resin and modified epoxy resin obtained has a residue of 63% and a viscosity of 8200 mPa.s/20°C. This resin solution cannot be diluted with water.

200 T of this resin solution are now mixed with 24.5 T of gluconic acid (47.5%). A pH of 6.1 is obtained. The resin is water-soluble and has a viscosity of 8000 mPa.s/20°C, with a residue of 60%. Further dilution with water gives colloid solutions which are suitable for use in 35

painting and lacquering. When diluted with water, the following viscosities and pH values are obtained:

	Residue %	Viscosity mPa.s/20°C	pH value
	60	5000	5.9
5	55	4600	5.8
	45	800	5.7
	35	70	5.6
	25	15	5.4

The colloid solution may be used as the inner coating for food cans and may be stoved at 190°C for 30 minutes. After stoving, the coating films with a thickness of 4 µm obtained by centrifugal coating are sterilisable and elastic. They do not impart any taste to the contents of the containers when used as an internal coating for food containers.

4) Colloid solution based on phenol-hydroxypropylphenol novolak and epoxy resin

a) Preparation of the methylol compound

1500 T of the polyphenol prepared as in Example 3a) are melted, mixed with 430 T of sodium hydroxide solution and 375 T of water and then cooled to 90°C. At this temperature, a total of 250 T of propylene oxide are added dropwise. The substance is immediately used up. After all the propylene oxide has been added, the mixture is cooled to 50°C, and whilst it is cooling 810 T of a 37% aqueous formaldehyde solution are added and the mixture is stirred at 50°C until, after 6 hours, the formaldehyde content has fallen to 0%. The resin is then mixed with 320 T of toluene and 960 T of butanol and adjusted to a pH of 4 with 695 T of 25% sulphuric acid. After the bottom liquor has been separated off, it is washed with 600 T of a half-concentrated sodium chloride solution, the second bottom

liquor is also separated off and dehydrated by distillation under reduced pressure, with recycling of the solvent. 450 T of water are separated off. The resin solution obtained is diluted to 60% with 369 T of isobutanol. The resulting resin solution has a viscosity of 700 mPa.s.

b) Preparation of the colloid solution

170 T of the phenolic resin solution obtained are freed from solvent over a water bath under reduced pressure as described in Example 3 and 60 T of ethylene glycol monoethyl ether are added. This solution is then mixed with 270 T of the solution of an amine-modified epoxy resin obtained according to paragraph 3 in Example 1. This solution is not water-dilutable and has a pH value of 7.08. After the addition of 50 T of 47.5% gluconic acid, a pH of 6.1 is obtained, with a residue of 56.2%. The viscosity is 2600 mPa.s/20°C. When the product is diluted with water, the following viscosities and pH values are obtained:

Residue %	Viscosity mPa.s/20°C	pH value
55	2070	6.0
45	1450	6.0
35	360	5.8
25	35	5.5

It is not intended that the examples given herein should be construed to limit the invention thereto, but rather they are submitted to illustrate some of the specific embodiments of the invention. Resort may be had to various modifications and variations of the present invention without departing from the spirit of the discovery or the scope of the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A dispersion being depositable by base or by electric
current comprising as the binder a self-hardening composi-
tion of
- I) A reaction product of A) at least one epoxy resin
based on diphenylolalkane and epihalohydrin having
an average molecular weight between 300 and 30,000
with C) a secondary amine which is thus present in the
reaction product as a tertiary amine and is converted
into a salt therein with D) and inorganic or monocarb-
oxylic acid and is further based on
- II) at least one phenolic resin B) in the form of a methy-
lol compound of substituted polyphenol compounds based
on a combination of substituted and unsubstituted phe-
nols on one hand, substituted with at least one sub-
stituent selected from the group consisting of alkyl,
alkenyl, aryl, aralkyl, monohydroxyalkyl or polyhy-
droxyalkyl, and formaldehyde on the other hand
- in a weight ratio of A) : B) of from 10 : 90 to 90 : 10,
said amine C) having been reacted in an amount of from 10
to 100 equivalent-% per epoxy group and the equivalent
ratio between the tertiary amine group and the acid being
(25 to 200) : 100.
2. A dispersion as claimed in claim 1 wherein its average
particle size is above the range between 10^{-4} and 10^{-6} mm
and it contains a reaction product of an epoxy resin A)
having an average molecular weight between 1000 and 30,000
or said dispersion represents a colloid solution contain-
ing a reaction product of resin A) having an average mole-
cular weight between 300 and 30,000.
3. A dispersion as claimed in claim 1, wherein the dis-
persions has a particle size above the range between 10^{-4}
and 10^{-6} mm and contains a dispersing agent.

4. A dispersion as claimed in claim 1 or 2 or 3, wherein
in the case of a dispersion with a particle size above the
range between 10^{-4} and 10^{-6} mm the phenol component of the
phenol resin B) contains at least one substituent selected
5 from the group consisting of alkyl, alkenyl, aryl and
aralkyl and in the case of a colloid solution the phenol
resin B) contains monohydroxyalkyl or polyhydroxyalkyl
groups as substituents, wherein the amount of said substi-
tuents is between 5 and 100 equivalent-%, referred to the
10 phenolic hydroxy groups.
5. A dispersion as claimed in claim 1 or 2 or 3, wherein
the amino component C) is a dialkanolamine or dialkylamine
having alkyl- or alkylene groups each with up to 3 C-atoms.
15
6. A dispersion as claimed in claim 1 or 2 or 3, wherein
component D) is a monocarboxylic acid containing hydroxy
groups.
- 20 7. A dispersion as claimed in claim 1 or 2 or 3, wherein
component D) is a monocarboxylic acid selected from the
group consisting of gluconic acid and lactic acid.
8. A dispersion as claimed in claim 1 or 2 or 3, wherein
25 in the case of a dispersion with a particle size above the
range between 10^{-4} and 10^{-6} mm contains a low-molecular
alcohol and in the case of a colloid solution contains a
glycol ether as a solvent.
- 30 9. A process for the preparation of dispersion as claimed
in claim 1 wherein the epoxy resin A) is reacted with the
secondary amine C) under formation of a tertiary amine
which is dissolved in at least one organic solvent and
converted to a salt with acid D) and wherein prior to, du-
35 ring or after the salt formation with the acid at least
one phenol resin B) is added, the solution obtained is ad-
mixed with water under dispersion and in the case of the
preparation or a dispersion with a particle size above the
range between 10^{-4} and 10^{-6} mm the organic solvent is sub-
0 sequently removed, the amine being reacted in an amount

between 10 and 100 equivalent percent per epoxy group and the equivalent ratio between the tertiary amino group and the acid is (25 to 200) : 100.

- 5 10. A process as claimed in claim 9 wherein the dispersion has a particle size above the range between 10^{-4} and 10^{-6} mm and contains a dispersing agent.
11. A process as claimed in claim 9, wherein in the case
10 of a dispersion with a particle size above the range between 10^{-4} and 10^{-6} mm the phenol component of the phenol resin B) contains at least one substituent selected from the group consisting of alkyl, alkenyl, aryl and aralkyl and in the case of a colloid solution the phenol resin
15 B) contains monohydroxyalkyl or polyhydroxyalkyl groups as substituents, wherein the amount of said substituents is between 5 and 100 equivalent-%, referred to the phenolic hydroxy groups.
- 20 12. A process as claimed in claim 9 or 10 or 11, wherein as amino component C) is dialkanolamine or dialkylamine is used, having alkyl- or alkylene groups each with up to 3 carbon atoms.
- 25 13. A process as claimed in claim 9 or 10 or 11, wherein component D) is a monocarboxylic acid containing hydroxy groups.
14. A process as claimed in claim 9 or 10 or 11, wherein
30 component D) is a monocarboxylic acid selected from the group consisting of gluconic acid and lactic acid.
15. A process as claimed in claim 9 or 10 or 11, wherein
35 in the case of a dispersion with a particle size above the range between 10^{-4} and 10^{-6} mm a low-molecular alcohol and in the case of a colloid solution a glycol ether is used as a solvent.

16. A coated article the coating of which has been obtained from a dispersion as claimed in claim 1 or from a dispersion prepared according to the process as claimed in claim 9.

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17. A coated article the coating of which has been obtained from a dispersion as claimed in claim 1 or from a dispersion prepared according to the process as claimed in claim 9, the coating of which has been obtained by electrodeposition.

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Abstract of the Disclosure

Dispersion based on self-hardening mixtures of

A) epoxy resins obtained from diphenylolalkane and epihalohydrin and

B) phenolic resins in the form of methylol compounds of substituted polyphenol compounds based on a mixture of substituted and unsubstituted phenols on the one hand and formaldehyde on the other hand, in a weight ratio of A) : B) of from 10 : 90 to 90 : 10, characterised in that the dispersion, which can be deposited by means of bases or electric current, contains a reaction product which has been prepared from an epoxy resin A) with an average molecular weight of from 300 to 30,000 with C) a secondary amine which is thus present in the reaction product as a tertiary amine and is converted into a salt therein with an inorganic or monocarboxylic acid D), the amine C) having been reacted in an amount of from 10 to 100 equivalent-% per epoxy group, whilst the equivalent ratio between the tertiary amine group and the acid is (25 to 200) : 100, process for preparing the dispersion and the use thereof in the production of coatings.

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